KnE Materials Science

TECHNOGEN-2019
IV Congress "Fundamental research and applied developing of recycling and utilization processes of technogenic formations"
Volume 2020

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Conference Paper

The Transformation of *Di-* and *Tri-*chloromethane Induced By Low Voltage Discharge

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Abstract

This article is focused on the transformation of di- and trichloromethane by induced low-voltage discharges in the liquid phase. To generate discharges, a direct current source is used (capacitance 2200 μF, voltage 60 V). The products and probable intermediates of the CH_2Cl_2 and $CHCl_3$ transformation were determined by the methods of thermodynamic modeling, FTIR spectroscopy and electron microscopy. Under the action of low-voltage discharges on the liquid substrates, needle fullerene-like structures are formed. In this case the gas phase consists mainly of hydrogen chloride. From the simulation of the nonequilibrium composition of particles and molecular systems it follows that in the course of induced reactions of CH_2Cl_2 and $CHCl_3$ and geminal elimination of HCl molecules, predominantly carbene-type intermediates are generated.

Keywords: dichloromethane, trichloromethane, low temperature plasma, discharges in the liquid phase.

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Published: 31 December 2020

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

The recent work is devoted to the new method development of the *di-* and *tri-*chloromethane fragmentation induced by the low voltage discharge in liquid phase and generation of number of intermediates. The results of recycling of chlorine contained industry wastes in useful products are presented. The improvement of the plasma chemical reactor design along with the programme control of a supply for the low voltage discharges was conducted [1]. The ways of the fragmentation of *di-* and *tri-*chloromethane as the poly-chloromethane components of chlorine-organic production by low voltage discharge in liquid phase are revealed [2].

The scheme of experimental equipment is shown in Figure 1. The reactor is made of Teflon and has 3 mm diameter cylindrical graphite electrodes. As the substrates the *di-*

and *tri*-chloromethane with purity 99.9% were used. The detailed description of our low discharge supply is presented previously [3].

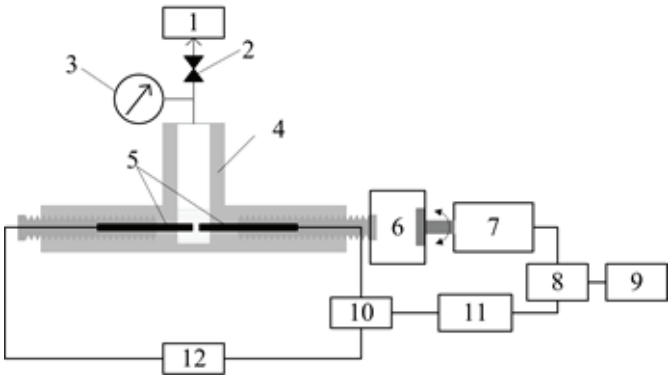

Figure 1: Schematic diagram of the setup: (1) gas collector, (2) valve, (3) pressure gauge, (4) reactor body, (5) electrodes, (6) coupling, (7) stepper motor, (8) stepper motor driver, (9) stepping-motor power supply, (10) current sensor, (11) microprocessor control system, and (12) power supply with capacitive energy storage

The direct current source with the following parameters, capacity 2200mkF, voltage 60V, current strength 2A for the discharge generating was used. The discharge pulses shapes were measured by oscilloscope Rigol DS 11047Z. The discharge curves of fragmentation for *di*-chloromethane are shown in Figure 2. The instantaneous value of power is calculated by multiplying the corresponding current and voltage values. Figure 2 shows that electrical discharges arise periodically with the current pulse time 5 ms.

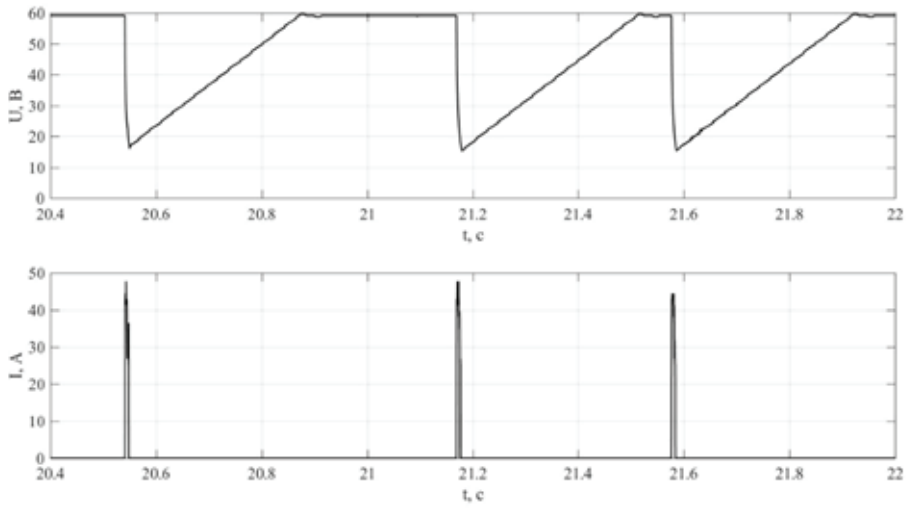

Figure 2: The waveform of single pulses.

The products of *di*- and *tri*-chloromethane fragmentation under low voltage discharge by simulation method were revealed and FTIR spectra were recorded by the IFS 1202 spectrometer. Electron microscopy was carried out by scanning electron microscope Tescan VEGA II. The microrelief was investigated at magnifications from

500x to 80,000x (80 kx). The survey was carried out at an accelerating voltage of 10 and 20 kV and a working distance of 3–9 mm; a backscattered electron detector (BSE) was used.

For the prediction of products composition of possible fragmentation ways by the plasma-chemical simulation of non-equilibrium intermediates and molecular ensembles as an example of chloroform transformation was conducted. Electrocontact plasma arises in the volume of liquid phase between the electrodes at the dielectric breakdown. When electrodes approach each other peculiar heterogenic system – the non-equilibrium plasma zone (gas bubble area) forms with its surrounding liquid and electrodes.

Plasma nonstationarity can be characterized by time stages: time of development; the time of exchange of electrodes by ions and electrons in an electronically activated medium; relaxation time mainly on the electrodes and in the surrounding fluid.

For the analysis of chemical and phase transformation in the indicated heterogenic system the model chemical plasma (MCP) [4] applicable for the equilibrium plasma was used. The generated plasma is non-equilibrium, because the high density of cathode electrons stream is determined by the corresponding electronic temperature, which is many times higher than the thermometrically measured temperature.

The simulation of similar plasma can be realized by the conception of conditionally equilibrium states [5], extended as necessary by the opportunities of MCP on the low temperature non-equilibrium plasma. For this the additional conditions in the Gibbs equation energy minimization method, which includes the determination of “redundant” non-equilibrium concentration value of electronic gas, were used.

The experimental data of the products composition of the chloroform fragmentation, forming under the low voltage discharge, allow to calculate the composition of chloroform discharge plasma (the detailed description is given in paper [2]). Graphical comparison of the observed chlorine molecule with a one grade less content of chlorine molecule, relative to hydrogen chloride, allow to evaluate the temperature of plasma formation as approximately 1000K. The non-equilibrium of the studied state is manifested by the relative concentration of electronic gas, which is equal to $\alpha=1\cdot10^{-5}$, corresponding to electronic temperature $T_e=1_{ev}$ or about 11600K.

In accordance to the obtained data of calculations for the fragmentation induced by discharge of chloroform dichlorocarben is generated basically as a result of geminal elimination from carbonchloride. The data are presented in [2] show that the content of this particles in low temperature plasma is maximal at 2000-2600K temperature range. At the further rise of temperature above 2600K the negligible decrease of their concentration is going on. Most probably diclorocarben transforms in two ways:

the recombination leading to formation of carbon tetrachloride and its telomerization products as well as its degradation with generating of two radicals (CCl·) and (Cl·).

The low voltage discharge on chloroform and *di*-chloromethane leads to an unusual direction of fragmentation. In the reaction of liquid di-chloromethane hydrogen chloride appears whereas in reaction of chloroform hydrogen chloride and some quantity of chlorine forms. The geminal elimination of hydrogen chloride is highly likely connected with generating of intermediates similar to carben type, for which the main direction of transformation is synthesis of needle and chemical bonded high porous structures.

Sufficient attention was attracted to revealing of the ways of di-chloromethane transformation induced by low voltage discharge. It should be noted that particles (CCl) are the source of carbon matter for the diamond films [6]. The transformation of di-chloromethane includes the elimination of hydrogen chloride and generating of carben type intermediates. “The assembly” of these particles leads to the forming of needle - shaped and chemically - bonded systems. Micro images of the surface of the obtained samples are presented in Figure 3.

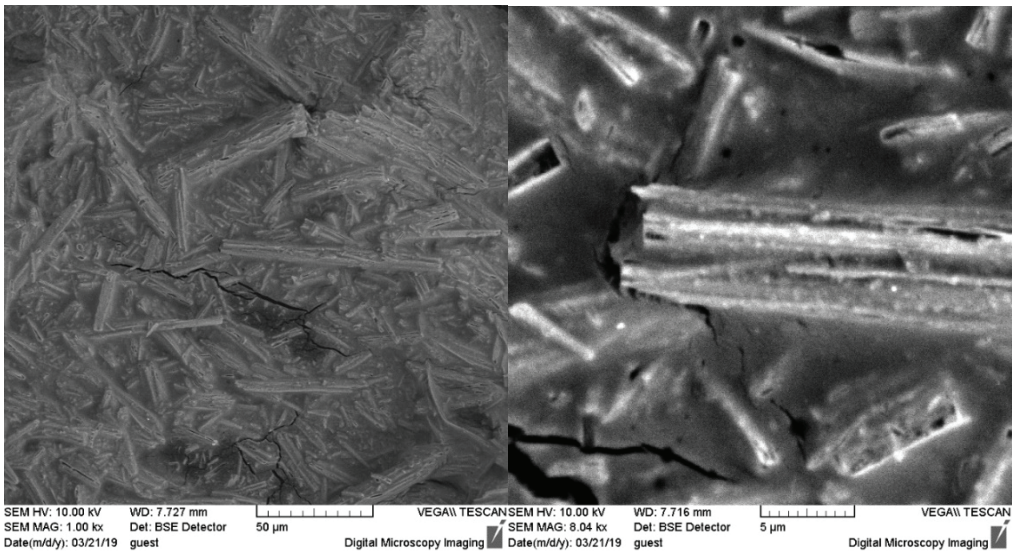

Figure 3: Electron microscopic image of the surface of the obtained samples.

The samples of products obtained by low voltage discharge reaction of *di*-chloromethane are highly dispersive black mixture deposited in di-chloromethane. The three variants of sample preparation for IR study were used: i) the IR spectra of liquid samples between the optical windows by the standard technique were recorded; ii) the liquid sample was deposited on the optical window with the lead gasket of 0.2 mm thickness and then by drying on air of the studied film samples were obtained for IR spectra procedure; iii) the IR spectra of KBr pallets containing the studied samples were recorded.

In the IR spectra of liquid samples, obtained in reactor without air access, the stretching vibration bands of (CCl) bond at 740 cm^{-1} and 705 cm^{-1}(shoulder) as well as the bending vibration band of angle (HCCl) at 1265 cm^{-1}, assigning to dichloromethane molecule, are shown. Besides the bands at 670 and 1216 cm^{-1} (Figure 4, labeled by asterisk) were observed. Two bands disappear in the spectra of the solid film at the evaporation of the solvent. At the same time in the spectra of these films the bands at 750, 764 (shoulder), 802, 1260 and 1275 cm^{-1} are shown, which are overlapped by bands of the initial dichloromethane in the liquid sample, but are visible in the spectrum of the solid film (Figure 5).

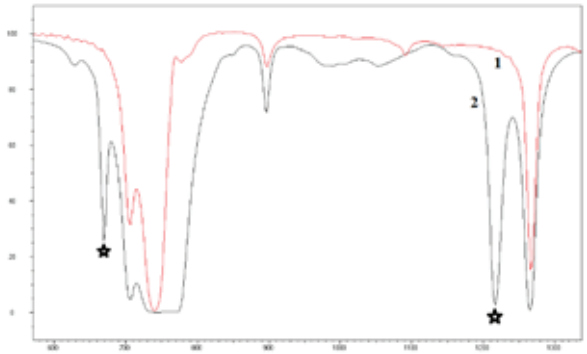

Figure 4: IR spectra of liquid product (2) and dichloromethane (1) in middle frequencies range.

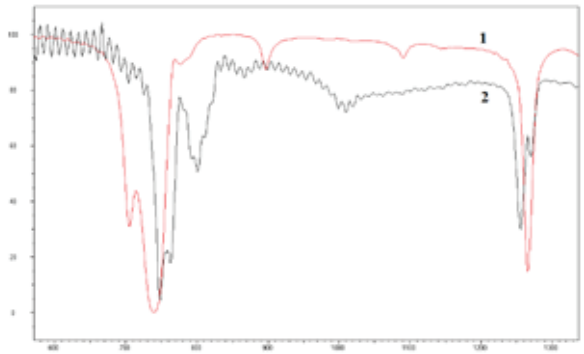

Figure 5: IR spectra of solid film (2) and dichloromethane (1) in middle frequencies range.

In the spectra of liquid samples, obtained in vacuum, in high frequencies region, along with stretching bands of (CH) bonds of dichloromethane at 2987 and 3055 cm^{-1}, a new band at 3021 cm^{-1} (Figure 6, labeled by asterisk) was observed. This one is absent in the spectrum of solid film.

In Figure 7 the IR spectra of chloroform and liquid product are presented.

Besides the bands of dichloromethane mentioned above, the bands at 1222, 1362, 1421 and 1713 cm^{-1} in the IR spectra of samples, obtained at air purge, are observed (in Figure 8 by asterisk are labeled the bands of dichloromethane and by arrow the bands of product).

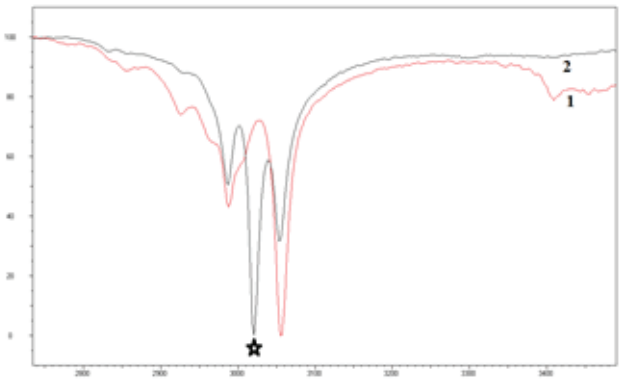

Figure 6: IR spectra of dichloromethane (1) and liquid product (2) in high frequencies region.

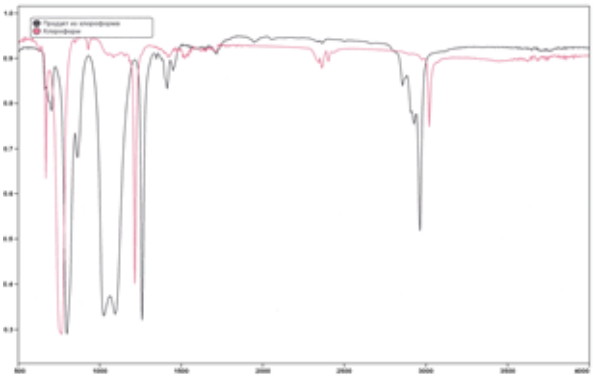

Figure 7: IR spectra of chloroform and liquid product.

These bands disappear in the spectra of the films, obtained at evaporation of solvent in the initial sample. In the spectra of films of the solid product, which forms in the reactor at small adding of air, the bands at 1016, 1096 cm^{-1} (In Figure 9, are labeled by asterisk) appear. These ones are not observed in the spectra of the product films, obtained in the reactor without air access (Figure 5).

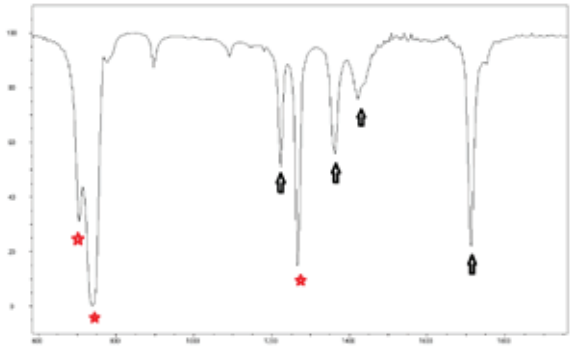

Figure 8: IR spectra of liquid product in middle frequencies region.

In spectrum of solid product, obtained at its concentrating from dichloromethane, recorded in KBr pallet, the bands at 800, 1020, 1095, 1262 и 2963 cm^{-1} (Figures 10,11) are observed.

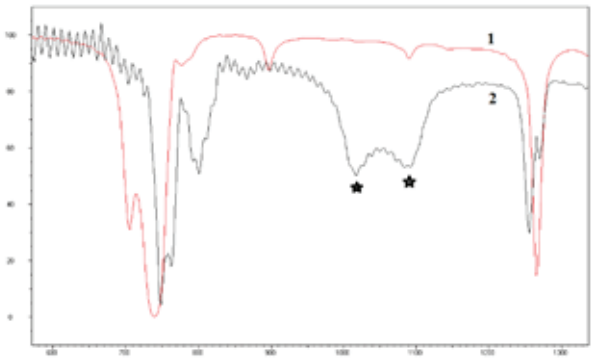

Figure 9: IR spectra of solid film (2) and dichloromethane (1) in middle frequencies range.

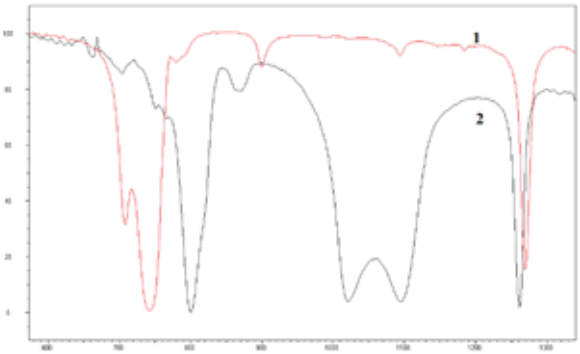

Figure 10: IR spectra of solid product (2) and dichloromethane (1) in middle frequencies region.

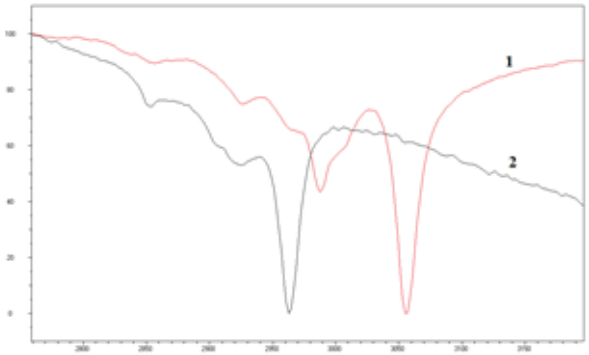

Figure 11: IR spectra of solid product (2) and dichloromethane (1) in high frequencies region.

The bands in the presented spectra are shown in typical regions, namely, in stretching vibrations region of (CCl) bonds (700-900 cm^{-1}), in stretching of (C-O) bond range (1100-1000 cm^{-1}), in bending vibration range of (HCCl) angle (1300-1200 cm^{-1}), stretching of (C-C) bond and bending of (HCC) angle vibration range (1500-1300 cm^{-1}), stretching vibration range of (C=O) bond and in stretching vibration range of (CH) bond (3100-2900 cm^{-1}). The presented assignment of the bands justifies that at non-oxygen conditions the product, containing carbon phase (needle structures and high porous shapes), as well as dichloromethane bonded with this phase, form. At the evaporation of fluid in the liquid product, bonded dichloromethane flies with the non-bonded dichloromethane, but in the solid film it the carbon phase only remains, which has in its structure (CCl)

and (CH) bonds. At oxidation of the carbon phase by air under low voltage discharge the volatile product, containing carbonyl group and hydrocarbon structure forms. In the solid film, of the liquid product, which forms in the reactor at small adding of oxygen, two bands of (C=O) stretching vibrations are observed. They can be assigned to symmetric and antisymmetric stretching vibrations in the (-COOC-) chain incorporated in the structure of carbon phase at its oxidation. The comparison of solid product spectra, recorded in KBr pallets, with the spectra of other samples confirms that the observed bands assign to the vibrations of stable carbon phase with the corresponding structure elements.

The IR spectrum, presented in Figure 7 indicates that chloroform generates active particles of carben type under low voltage discharge, which lead to chemical bonded shapes, characteristic for carben containing fragments.

Acknowledgment

The reported study was funded by RFBR according to the research project № 18-29-24008.

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